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XVII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

Presented by Josiah P. Cooke, Director, March 9, 1887.

A DETERMINATION OF THE RELATION OF THE ATOMIC WEIGHTS OF COPPER AND SILVER.

By Theodore W. Richards.

In the Report of the Committee on Electrolysis made to the British Association at Birmingham, of which an advance copy has been received by Professor Cooke through the kindness of Dr. Oliver Lodge, a direct determination is given of the ratio between the atomic weight of copper and that of silver, based on the electrolytic experiments of W. N. Shaw. As the value of the ratio thus obtained is quite different from that usually accepted, it seemed to Professor Cooke desirable that the results should be confirmed by a direct chemical method, and the writer was intrusted with this investigation.

Of the work worthy of consideration which has thus far been done upon the atomic weight of copper, first in chronological order comes that of Berzelius,* who made two determinations of the weight of copper formed by the reduction of pure cupric oxide by hydrogen. He found the percentage of copper in this compound to be 79.823 ± .002. This corresponds to an atomic weight of 63.153, taking oxygen $= 15.963$, with Clarke. The next determination was by Erdmann and Marchand,† who used the same method. They found the percentage of copper in cupric oxide to be 79.8645 ± .0038 as a mean of four determinations, — a value which makes $Cu = 63.316$. Millon and Commaille,‡ in three determinations, — which did not, however, closely agree with one another, — found the relation, CuO : Cu = 100 : 79.7787; and calculating from this relation the atomic weight of copper, the value 62.979 is obtained. Dumas * made several determinations of the reduction of cupric oxide and the synthesis of cuprous sulphide; and calculates the value Cu = 63.5.

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* Poggend. Annal., viii. 177.

† Journ. für Prakt. Chem., xxxi. 389. 1844.

‡ Fresenius' Zeitschrift, ii. 475. 1863.

Hampe,† whose work gave the most concordant results thus far secured, obtained from three determinations of the percentage of copper in cupric oxide the mean value of 79.8347 ± .0013; and from two analyses of anhydrous cupric sulphate by electrolytic precipitation he found the proportion $CuSO_4$: Cu = 100 : 39.725 ± .0007. The atomic weights of copper from these two methods are respectively 63.197 and 63.173.

This was in 1874; and the subject has rested undisturbed until last year, when W. N. Shaw, in the paper before referred to, sought to prove the accuracy of Faraday's law of electrolysis in atomic proportions, by means of the actual weights of silver and copper deposited in cells in the same circuit. For the particulars of his method the Report of the Committee on Electrolysis should be consulted; it is sufficient here to say that as the mean of many determinations he finds the ratio of the silver and copper precipitated to be 3.39983 : 1. Correcting this result for variations in current density, he obtains the value 3.39888, and finally adopts the practically identical value 3.400, which makes the ratio Ag : Cu = 17 : 10. This last value makes Cu = 63.333, while the corrected value gives as the atomic weight the quantity 63.360.

Below is a summary of all the results : —

Berzelius, from CuO	63.153
Erdmann and Marchand, from CuO	63.316
Millon and Commaille, from CuO	62.979
Dumas, from CuO and Cu_2S	63.5
Hampe, from CuO	63.197
" from $CuSO_4$	63.173
W. N. Shaw, by relation to silver	63.333
" " " corrected	63.360

The most obvious chemical method for the determination of the relation of the atomic weights of silver and copper, is by the precipi-

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* Ann. d. Chim. et Phys., (3,) lv. 129.

† Fresenius' Zeitschrift, xiii. 352. 1874.

tation of silver from a solution of a pure silver salt by means of pure copper; and this was the method adopted in the present determination. Hampe, in his work on the atomic weight of copper, attempted the same method, but rejected it for two reasons, — the first being that the silver dissolved, or appeared to dissolve, to a slight extent in the hot water used for washing; and the second being that it was impossible to prevent copper from coming down with the silver, no matter how long the precipitate was digested with the argentic nitrate solution. As will be seen, however, both of these difficulties have been entirely overcome.

The silver salt selected for the precipitation was the nitrate, on account of its ready crystallization, its easy solubility in water, and the facility with which it can be obtained pure. For the preparation of the salt used in the work, ordinary pure argentic nitrate was crystallized many times from hot water, and finally fused for two hours in an air-bath kept at 205° C., — a few degrees above its melting point. This preparation was a white translucent substance interspersed with transparent crystals, dissolving completely in water and giving a colorless solution which was wholly neutral.

The copper used was prepared by electrolysis from cupric sulphate, through the kindness of Mr. Wilson, of the University Press. It was cut into small pieces, and these were digested in succession with weak potassic hydrate, dilute sulphuric acid, and then a very large amount of water. The copper was then boiled with water for about half an hour and washed with a large amount of distilled water, then dried and reduced at a low red heat by means of perfectly pure hydrogen, and allowed to cool in a stream of the gas. The metal thus prepared had a beautiful red metallic lustre, and showed no trace of oxidation after keeping a month. Before use it was dried in an air-bath at 110°, allowed to cool in a desiccator, and weighed by itself on a balance which was distinctly sensible to a twentieth of a milligram. In addition to receiving the treatment described above, the copper used in the fifth and sixth experiments was oxidized in a stream of pure air for half an hour, and then again reduced by hydrogen; but the concordance of those two results with the others shows that this precaution was not necessary.

In a few preliminary experiments it was found that on the temperature of the solution, and on the temperature alone, depended the regularity with which the silver was precipitated by the copper. At 90° the deposition is very rapid, nitrous fumes are evolved, and a large amount of copper comes down with the silver. As the temperature of the solutions used is lower, the reaction becomes less rapid, and the amount of copper deposited with the silver less, until at ordinary temperatures it is comparatively small; and below 0° the silver comes down absolutely pure, and not the least evolution of gas is observed. One of the difficulties of Hampe can then be overcome by keeping the beaker containing the solution in a freezing mixture; and the perfect definiteness of the reaction, which before might have been questioned, is thus established. The duration of the reaction at —1° is from twelve to twenty-four hours, according to the dilution of the argentic nitrate. The more dilute the solution is, the longer the precipitation takes, and the more finely divided is the deposited silver; but when the solution is very concentrated, the reaction is completed in a comparatively short time, and the silver comes down in a beautiful compact crystalline crust which takes the form of the copper.

The silver which was formed was collected in a Gooch crucible and washed with cold water, of which less than 250 c. c. were necessary to give a filtrate in which no trace of silver or copper could be detected.

The fact that the determinations given below agree so exactly with each other is of itself proof that no silver was dissolved, — first, because the precipitate in the different experiments was of very different degrees of fineness; and secondly, because the precipitate in each experiment was washed with a different amount of water, the silver of the last experiment having at least four times as much water passed over it as that of the first. And the fact that the results are not affected by either circumstance shows clearly that no perceptible amount of silver could have been dissolved; for if so, the loss must have varied both with the condition of the precipitate and with the amount of the wash-water. The different result obtained by Hampe was probably the effect of hot water on a very finely divided precipitate.

The silver, whether in crystalline plates or in crystalline powder, formed a very convenient precipitate with which to work; it was easily transferred and easily washed, did not adhere to the glass, and was in every way adapted for quantitative work.

The conditions of the following experiments as regards the quantity of water and the excess of argentic nitrate used above the amount required to dissolve the copper, were varied as much as possible. In some determinations barely enough of the argentic nitrate was used to effect the solution; while in others the excess of the silver salt amounted to nearly two grams. The time allowed the reactions was also varied from twenty-four to seventy-two hours.

Relation of Silver to Copper.

No. of Expt.	c. c. H_2O used.	Weight Cu taken.	Weight Ag formed.	Equivalent $Ag_2 : Cu = 1 : n$.	Atomic Weight Cu $Ag = 108$.	Atomic Weight Cu $Ag = 107.675$.
1	20	0.53875	1.8292	0.29452	63.618	63.427
2	25	0.56190	1.9076	0.29456	63.624	63.432
3	120	1.00220	3.4016	0.29462	63.639	63.447
4	30	1.30135	4.4173	0.29462	63.638	63.447
5	20	0.99870	3.39035	0.29457	63.628	63.437
6	25	1.02050	3.4646	0.29456	63.623	63.434
			Average,	0.29457	63.628	63.437

The mean value, 63.437, has a greatest variation of ±.01, and a probable error of ±.0023.

The value obtained by Shaw was	63.333
" " " corrected	63.360
The value given by Clarke is	63.173

It remains only to prove the absolute purity of the copper used and the silver formed. The only metals which could affect the atomic weight of copper to an appreciable extent, if present in traces, are bismuth and silver. The former was tested for with great care, using a delicate spectroscope, and not the faintest trace of the very well-defined blue bismuth line was apparent; further, ten grams of the copper were dissolved in nitric acid, a little potassic hydrate added to the diluted solution, and the whole boiled and shaken for three hours. According to Hampe, all the bismuth present will be found in the basic precipitate; this was tested qualitatively for the metal, and not a trace was found. The solution of a portion of the copper in pure nitric acid gave not the faintest trace of opalescence with hydrobromic acid, excess of ammonic hydrate, or baric chloride. A gram of the copper was tested for arsenic and antimony in a Marsh-Berzelius apparatus, and no trace of a mirror was obtained. As the presence of so much copper would cause the generator to run too rapidly, the solution was treated with just enough potassic ferrocyanide to effect precipitation, and the colorless filtrate was run into the apparatus. This method has been found to give good results. The copper and the precipitated silver each dissolves in nitric acid without leaving a trace of residue.

If the copper is pure, the only possible impurity which the silver could contain is copper; and this was tested for with great care in each precipitate by dissolving one to two grams in nitric acid and adding excess of ammonic hydrate. In no case was the slightest blue color noticed; and as under the same circumstances a tenth of a milligram of copper gave a distinct bluish tinge, it may be assumed that the silver contained no copper. This method is a convenient one for the preparation of chemically pure silver, and avoids the necessity of fusion and the concomitant absorption of oxygen and possible admixture of silicic anhydride.

Although the value of the atomic weight of copper obtained, 63.44, does not exactly coincide with Shaw's results, it is at least very much nearer to them than is the old accepted value of 63.17 ; especially if we take his result as corrected for current density. The new value is very nearly that found by Dumas from cuprous sulphide, and it falls within the limits assigned by L. Meyer and Seubert as the possible error of the accepted value.